

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
27 September 2001 (27.09.2001)

PCT

(10) International Publication Number
WO 01/70893 A2

(51) International Patent Classification⁷: **C09D 167/00**

Henry; 2446 Baylor Circle, North Canton, OH 44720 (US).

(21) International Application Number: PCT/EP01/03441

(22) International Filing Date: 23 March 2001 (23.03.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/192,111 24 March 2000 (24.03.2000) US

(71) Applicant: **SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.** [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(72) Inventors: **SMITH, Oliver, Wendell**; 242 Wildwood Trail, Petal, MS 39465 (US). **THAMES, Shelby, Freland**; 103 Darby Road, Hattiesburg, MS 39401 (US). **ZHOU, Lichang**; 184 Princeton Arms, Cranbury, NJ 08512 (US). **FORSCHNER, Thomas, Clayton**; 2211 Woodland Drive, Richmond, TX 77469 (US). **BOON, Wyndham**,



WO 01/70893 A2

(54) Title: CARBOXYL-FUNCTIONAL POLYESTER EPOXY RESIN POWDER COATINGS BASED ON 1,3-PROPANEDIOL

(57) Abstract: A polyester powder coating composition formed by reacting: a) a polyester resin formed by reacting one or more aliphatic glycols and one or more polycarboxylic acids and/or anhydrides, wherein the aliphatic glycol is comprised of 5 to 90% 1,3-propanediol on a molar basis, in the presence of an esterification catalyst and then endcapping the polyester with an endcapping agent to ensure that the polyester has carboxyl chain ends; and b) an epoxy resin crosslinking agent.

CARBOXYL-FUNCTIONAL POLYESTER EPOXY RESIN POWDER
COATINGS BASED ON 1,3-PROPANEDIOL

FIELD OF INVENTION

The present invention relates to an epoxy resin crosslinked polyester powder coating. More particularly, the present invention relates to the modification of the polyester typically used in carboxyl functional polyester-epoxy coatings with 1,3-propanediol (1,3-PDO) for significantly improved flexibility and impact resistance, with other key properties unchanged over a broad range of 1,3-PDO concentrations. In addition, the 1,3-PDO modified polyester has lower melt viscosity than polyesters made with 100% neopentyl glycol.

BACKGROUND OF THE INVENTION

The development of powder coatings has become increasingly significant in recent years. Powder coatings release no harmful solvents during application, may be applied in a highly efficient manner with little waste, and, thus, are considered particularly environmentally friendly and economical. Usable powder coatings may be obtained using curable epoxy resin powder coatings. Many epoxy resin powder coatings currently commercially available contain solid polyester polyols which are cured with epoxy resins.

Polymers used in the manufacture of powder coatings are classified broadly as either thermosetting or thermoplastic. Thermosetting coatings, when compared to

coatings derived from thermoplastic compositions, generally are tougher, more resistant to solvents and detergents, have better adhesion to metal substrates, and do not soften when exposed to elevated temperatures.

5 However, the curing of thermosetting coatings has created problems in obtaining coatings which have, in addition to the above-stated desirable characteristics, good smoothness, and flexibility.

Thermoset powder coatings can be grouped into epoxy, epoxy-polyester, polyester-urethane, TGIC polyester, and acrylic. Epoxy-polyester coatings have better colour retention and UV resistance than epoxy powder coatings. Such coatings are widely used in household equipment such as refrigerators, freezers, washing machines, stoves, and other kitchen equipment, metal furniture, ceiling panels for the building industry, shower cabinets, automotive components, agricultural equipment, and machinery, engineering, and electrical parts.

Coatings derived from thermosetting coating compositions should possess good impact strength, hardness, flexibility, and resistance to solvents and chemicals. For example, good flexibility is essential for powder coating compositions used to coat sheet (coil) steel which is destined to be formed or shaped into articles used in the manufacture of various household appliances and automobiles where the sheet metal is flexed or bent at various angles.

Powder coating systems based on carboxyl polyesters such as neopentyl glycol based carboxyl polyesters and melamine-, benzoguanamine-, and urea-formaldehyde cross-

linking agents have been used in the coatings industry. See, for example, those described in US-A-5739204. EP-A-0008344 discloses a similar system and mentions the use of 1,3-PDO.

5 Neopentyl glycol is often used in formulations for polyester powder coatings along with a mixture of terephthalic and isophthalic acids either by themselves or as mixtures and optionally branched with small amounts of trimethylol propane. Typically when the polyester
10 used in this type of powder coating is modified for improved flexibility, impact, and toughness, then other properties of significance to the coating are compromised. Other potential modifiers include adipic acid, 1,4-butanediol, and 2-methyl-1,3-propanediol.

15 There does not appear to be any reference in the art which suggests the incorporation of 1,3-propanediol into a carboxyl functional polyester epoxy resin powder coating composition for increased impact resistance and flexibility without the loss of other critical properties
20 and also where the 1,3-PDO modified polyester has lower melt viscosity than polyesters made with 100% neopentyl glycol.

SUMMARY OF THE INVENTION

25 In accordance with the foregoing, the present invention comprises a polyester powder coating composition formed by reacting:

- a) a polyester resin formed by reacting one or more aliphatic glycols and one or more polycarboxylic acids and/or anhydrides, wherein the aliphatic glycol
30 is comprised of 5 to 90% 1,3-propanediol on a molar

basis, in the presence of an esterification catalyst and then endcapping the polyester with an endcapping agent to ensure that the polyester has carboxyl chain ends; and

- 5 b) an epoxy resin crosslinking agent.

It has now been demonstrated that by partially replacing the neopentyl glycol with 1,3-propanediol the formulation exhibits improved impact resistance and flexibility with other key properties essentially
10 unchanged over a broad range of 1,3-propanediol concentrations and also that the 1,3-PDO modified polyester has a lower melt viscosity than polyesters made with 100% neopentyl glycol.

In accordance with the present invention there is
15 also provided a polyester powder coating composition formed by reacting:

- a) a polyester resin formed by reacting a mixture of neopentyl glycol and 1,3-propanediol, wherein the 1,3-propanediol comprises from 5 to 90% of the
20 mixture on a molar basis, with a mixture of terephthalic acid and isophthalic acid, wherein the ratio of terephthalic acid to isophthalic acid is in the range of 90/10 to 50/50, in the presence of dibutyl tin oxide, and adding
25 trimellitic anhydride to endcap the polyester; and
- b) an epoxy resin crosslinking agent which is a diglycidyl ether of 2,2-bis(4-hydroxy phenyl) propane which has been reacted with bisphenol-A
30 and has a weight per epoxy of 450 to 900.

In accordance with the present invention there is further provided any coated product made using the powder coating composition of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

5 The present invention will now be described by way of example with reference to the accompanying drawings, in which:-

Figure 1 is a graph showing the glass transition temperatures of the various formulations;

10 Figure 2 is a graph showing the Differential Scanning Calorimetry (DSC) curves of carboxyl polyester resins;

Figure 3 is a graph showing the Differential Scanning Calorimetry (DSC) curves of polyester/epoxy hybrid powder coatings; and

15 Figure 4 is a graph showing the gloss of clear and pigmented polyester/epoxy powder coatings.

DETAILED DESCRIPTION OF THE INVENTION

In the present invention it has been found that replacing the aliphatic glycol, which preferably is
20 neopentyl glycol (NPG), with from 5 to 90%, preferably 10 to 50%, 1,3-propanediol (1,3-PDO) on a molar basis provides significant improvements in the impact resistance and flexibility of epoxy resin crosslinked polyester powder coatings, while other properties were
25 about the same as noted in a control using 100% NPG; and also the 1,3-PDO modified polyester has a lower melt viscosity than polyesters made with 100% neopentyl glycol. Properties of carboxyl capped polyesters that were examined were carboxy equivalent, acid number,
30 colour before grinding, glass transition temperature

(T_g), processability, storage stability, front/reverse impact, powder flow properties, powder reactivity, hardness, adhesion, MEK double rub, and chemical and stain resistance.

5 The preferred carboxyl capped polyesters are characterized by an acid number of 30 to 120 mg KOH/g, preferably 40 to 110 mg KOH/g, and a T_g of greater than 40°C. The acid number = 56,100/equivalent weight (56,100 is the weight in mg per mole KOH). Low equivalent or
10 high acid number results in high crosslinking density and brittleness, while high equivalent or low acid number results in low crosslinking density, and thus poor performance such as low methylethylketone and solvent resistance, etc. The T_g range is generally a requirement
15 for good storage stability.

 The starting materials for the polyester of the present invention are aliphatic glycols including 1,3-PDO, aromatic polycarboxylic acids or anhydrides, an esterification catalyst, and optionally a branching
20 agent. The starting materials for the cured coatings of the present invention are the 1,3-PDO containing polyester, one or more epoxy resins, a crosslinking catalyst and optionally conditioning agents, auxiliary agents, and additives.

25 Suitable aliphatic glycols have a number average molecular weight of 62 to 500 and may optionally contain ether groups, ester groups, and/or carbonate groups. Suitable aliphatic glycols include, but are not limited to, ethylene glycol, 1,2-propanediol, 2-methyl-1,3-
30 propanediol, 1,3- and 1,4-butanediol, 1,6-hexanediol,

diethylene glycol, dipropylene glycol, neopentyl glycol and mixtures of these diols. Other suitable diols include triethylene glycol, tetraethylene glycol, tripropylene glycol, tetrapropylene glycol, polycarbonate diols having hydroxyl numbers of about 56 to 168, dimeric fatty alcohols and mixtures of these diols. The reactive hydroxyl component (carboxyl, amide) can be simple monomeric units or oligomeric units or low molecular weight polymeric units. The preferred glycols are aliphatic glycols such as 1,3-butylene glycol or 1,4-butylene glycol; ethylene glycol and propylene glycols; and neopentyl glycol. Neopentyl glycol was most preferred and used in the examples herein. Also useful is a minor amount of a trihydric or higher alcohol as will be discussed below.

Suitable acids include saturated, unsaturated, aliphatic, or aromatic polycarboxylic acids and/or anhydrides such as phthalic, isophthalic, terephthalic, sebacic, maleic, fumaric, succinic, adipic, azelaic, malonic, dodecanedioic, trimellitic, pyromellitic, and similar polycarboxylic acids, or mixtures thereof. The polycarboxylic acids and/or anhydrides preferred in the present invention are isophthalic, terephthalic, and trimellitic used individually or mixed. It is preferable to use the acid form in this reaction step. Most preferred is a mixture of terephthalic acid to isophthalic acid in a molar ratio of 90/10 to 50/50.

A branching agent is also useful, such as, for example, a small amount of a triol or higher alcohol. Suitable branching agents include, but are not limited to

trimethylolethane, trimethylolpropane, or pentaerythritol. The preferred was trimethylolpropane.

The carboxyl functional polyesters of the present invention may be synthesized by a two stage process. This is an esterification reaction. In the first stage, dibasic acid such as terephthalic acid (TPA), isophthalic acid (IPA), polyols such as NPG and PDO diols, and optional branching agents like trimethylolpropane are reacted at a temperature in the range of 150 to 250°C, preferably 170 to 230°C, to form a hydroxyl-terminated prepolymer.

In the second stage, the hydroxyl groups are endcapped with carboxylic acids or their anhydrides to form an acid polyester. The amount of endcapping agent used is determined by the hydroxyl number of the polyester. From 80 to 100% of the stoichiometric amount required to cap all of the chain ends of the polyester is generally added. The endcapping agents which can be utilized are generally acids or anhydrides containing a plurality of carboxylic acid groups, that is two or more carboxylic groups per molecule. Suitable acids include saturated, unsaturated, aliphatic, or aromatic dicarboxylic acids such as phthalic, isophthalic, terephthalic, sebacic, maleic, fumaric, succinic, adipic, azelaic, malonic, dodecanoic, trimellitic, pyromellitic, or mixtures thereof. Terephthalic acid is preferred with isophthalic acid being highly preferred. Anhydrides of these acids, if there are any, can also be used as endcapping agents and are preferred, including the anhydrides of the acids described above, and especially

including phthalic anhydride, trimellitic anhydride and succinic anhydride, wherein trimellitic anhydride is preferred. The endcapping agent is added to the prepolymer and the esterification is continued until a desired acid number is obtained. The total reaction time is approximately 10 to 15 hours.

A conventional catalyst for promotion of an esterification reaction, such as dibutyltin oxide, can be used in catalytic amounts of 0.01 to 1 wt%. The catalyst can be added in either Stage 1 or Stage 2. Catalysts which can be for the esterification include tin, antimony, titanium, and zirconium compounds, such as titanium alkoxides and derivatives thereof, such as tetra(2-ethylhexyl)titanate, tetrastearyl titanate, diisopropoxy-bis(acetylacetonato) titanium, di-n-butoxy-bis(triethanolaminoato)titanium, tributyl monoacetyltitanate triisopropyl monoacetyltitanate and monoacetyltitanate; titanium complex salts such as alkali titanium oxalates and malonates, potassium tetrabenzoic acid titanate; titanium complexes with hexafluorotitanate and titanium complexes with hydroxycarboxylic acids such as tartaric acid, citric acid or lactic acid, catalysts such as titanium dioxide/silicon dioxide coprecipitate and hydrated alkaline-containing titanium dioxide; and the corresponding zirconium compounds.

Xylene/water can be added before the reaction starts to facilitate the removal of water formed during the reaction. In the examples, 1,3-propanediol was substituted for neopentyl glycol in molar increments of 0, 15, 30, 50, and 100%.

There are alternative ways of carrying out the reaction, as will be apparent to those skilled in the art. A commercial scale reaction would probably rarely use xylene/water and could start with an ester, such as dimethylterephthalate (DMT) or dimethylisophthalate (DMI). It is also possible to use acid chlorides.

Powder coatings may be prepared from the 1,3-propanediol derived polyesters formulated with an epoxy resin crosslinking agent, a flow control agent, and a crosslinking catalyst. Conventional pigmenting materials (pigments or dye), such as titanium dioxide, may also be included in the formulation to impart a desirable colour to the coated substrate.

Epoxy resins suitable for the invention composition are generally any epoxy resins which are solid at room temperature. The epoxy resin preferably has an average weight per epoxide (WPE) within the range of 400 to 1400 and a number average molecular weight within the range of 800 to 5000. More preferably, the epoxy resin has a WPE of 500 to 1000 and a number average molecular weight of 1000 to 2000. Higher WPE's and molecular weights may be used, provided that the resin is blended at the processing temperature and processable in a high shear mixer or a melt blender.

Generally the epoxy resin will have a 1,2-epoxy equivalency greater than one and preferably about two or more. The epoxy resin may be saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic. Examples of epoxy resins suitable for use in the present invention include polyglycidyl ethers of polyhydric

compounds, brominated epoxies, epoxy novolacs or similar polyhydroxyphenol resins, polyglycidyl ethers of glycols or polyglycols, and polyglycidyl esters of polycarboxylic acids. Preferably the epoxy resin is a polyglycidyl ether of a polyhydric phenol. Polyglycidyl ethers of polyhydric phenols can be produced, for example, by reacting an epihalohydrin with a polyhydric phenol in the presence of an alkali. Examples of suitable polyhydric phenols include: 2,2-bis(4-hydroxyphenyl) propane (bisphenol-A); 2,2-bis(4-hydroxy-tert-butylphenyl) propane; 1,1-bis(4-hydroxyphenyl) ethane; 1,1-bis(4-hydroxyphenyl) isobutane; 2,2-bis(4-hydroxytertiarybutylphenyl) propane; bis(2-hydroxynaphthyl) methane; 1,5-dihydroxynaphthalene; and 1,1-bis(4-hydroxy-3-alkylphenyl) ethane. The preferred polyhydric phenol is bisphenol-A. A preferred epoxy resin is a diglycidyl ether of 2,2-bis(4-hydroxyphenyl) propane which has been reacted with bisphenol-A and has a weight per epoxy of 450 to 900. Commercial examples of suitable epoxy resins include advanced EPON (trade mark) Resin 828, a product of Shell Chemical Company, which is a diglycidyl ether of 2,2-bis(4-hydroxyphenyl)propane having an average molecular weight of 380 and a weight per epoxy in the range of 180 to 195. The preferred crosslinking agents are EPON Resins 1001F, 1002F, and 2002, which are advanced EPON 828 resins reacted with bisphenol-A which have a weight per epoxy of 450 to 900.

A flow control or levelling agent is desirably incorporated into the coating formulation to aid in levelling the applied and thermoset coatings. Such flow

control agents typically comprise acrylic polymers and are available from several suppliers, i.e., MODAFLOW from Monsanto Company, BYK 360P from BYK Mallinkrodt and ACRONAL from BASF. A suitable concentration range for
5 incorporation of the flow control agent into the coating is 0.25 to 2.0% based on the weight of the resin solids, and preferably in the range of 0.60 to 1.5%.

The powder coatings can be cured or crosslinked without the use of a catalyst. However, it has been
10 found to be a practical necessity to include a catalyst to promote the crosslinking reaction of the epoxy resin with the polyesters. The uncatalyzed rate of reaction has been found to be too slow to suit the baking schedules established in the industry. Suitable
15 catalysts include amine containing compounds, such as amides, imides, imidazoles, quaternary ammonium salts, phosphonium salts, metal salts of acidic and fatty acids, tin and zinc compounds. Specific samples of these catalysts are tetrabutylammonium and choline chloride.
20 These catalysts may be used either alone or in combination. Further, as the kind and amount of the catalyst to be used are variable depending on the kind and amount of the resin and the curing conditions, careful selection is necessary to meet the required
25 performance. A suitable concentration range for incorporation of the catalyst into the coating is 0.01 to 1% based on the weight of the resin solids, and preferably in the range of 0.05 to 0.5%.

EXAMPLES

Synthesis of Carboxyl Functional Polyesters.

A two-stage process was used for the synthesis of carboxyl functional polyesters. In stage 1, terephthalic acid (TPA), isophthalic acid (IPA), NPG and PDO were reacted at 170 to 230°C in a 1 litre round bottom flask under nitrogen to form a prepolymer. In stage 2, trimellitic anhydride (TMA) was added and the esterification was continued to an acid value of 100 to 110. The total reaction time was approximately 10 to 15 hours. Dibutyltin oxide (0.4%) as used as a catalyst and xylene/water were added to facilitate the removal of water formed during the reaction. Polyester compositions with molar substitutions of PDO for NPG from 0 to 100% are listed in Table 1.

Table 1

Mole Composition of the Carboxyl Functional
Polyester Resins

Set	CPE00	CPE15	CPE30	CPE50	CPE100
NPG/PDO (mole)	100/0	85/15	70/30	50/50	0/100
Terephthalic Acid (TPA)	1.376	1.397	1.426	1.461	1.556
Isophthalic Acid (ITA)	0.344	0.349	0.357	0.365	0.349
Neopentyl Glycol (NPG)	1.894	1.670	1.369	1.000	0.000
1,3-Propanediol (PDO)	0.000	0.251	0.587	1.000	2.116
Trimellitic Anhydride (TMA)	0.349	0.348	0.346	0.346	0.343

Preparation of Powder Coatings.

Polyester/epoxy hybrid powder coatings were prepared from the PDO derived polyesters formulated with epoxy resin via equal equivalents of carboxyl/epoxy groups. EPON 1001F Resin from Shell Chemical Company, having an equivalent weight of 525-550, was used as a crosslinking agent for the polyesters. EPON 1001F Resin has very low

equivalent weight among the commercial available epoxy resins. 0.2% Choline chloride, Actiron CC-6 from Synthron, Inc., was used as a catalyst. A flow control agent (Modaflow Powder III, Monsanto) and a degassing agent, benzoin (Uraflow-B, GCA Chemical Corporation) were also incorporated into the coatings. Pigmented powder coatings were prepared by using R-960 TiO₂ (DuPont) at a pigment/binder ratio of 0.7/1 by weight. The final powder coating compositions are listed in Table 2.

All the ingredients were initially premixed in a high speed mixer for 2 minutes to assure homogeneous mixing and the solids were then fragmented into small particles. The resulting intimate mixture was then continuously processed through a twin screw extruder to produce a uniform viscous melt. The extrusion temperature was maintained at 75°C in zone 1 and 80°C in zone 2 at 50 rpm. The molten extrudates were passed through a pair of water cooled squeeze rolls to yield a friable product. The products were then pulverized using a hammer mill with liquid nitrogen fed slowly into the grinding chamber.

The final powders were electrostatic-spray applied to grounded cold-rolled steel panels (Q Panel QD-36 and S-36) and the coating properties were evaluated after curing at 190°C for 15 minutes. The curing was carried out by placing panels in a hot air oven.

Table 2
Powder Coatings formulations

Set	CPE00	CPE30	CPE50	P-CPE00	P-CPE30
CPE00	48.65	--	--	28.55	--
CPE30	--	49.38	--	--	28.98
CPE50	--	--	49.38	--	--
EPON 1001F Resin	49.48	48.75	48.75	29.04	28.61
DuPont R-960 TiO ₂	--	--	--	40.31	40.31
Choline Chloride	0.20	0.20	0.20	0.20	0.20
ModaflowPowder III	1.18	1.18	1.18	1.15	1.15
Benzoin	0.49	0.49	0.49	0.75	0.75
Total	100	100	100	100	100

Characteristics of Polyester Resins.

5 The carboxyl functional polyester resins derived from PDO afforded properties similar to those based on NPG (Table 3). The glass transition temperatures (T_g) of the polyesters decreased with increasing PDO contents (Figure 1). For example, the T_g values ranged from 67°C for the

10 NPG polyester to 55°C for the 50% PDO polyester. Glass transition temperatures for the carboxyl functional polyesters were 6 to 8 degrees higher than the corresponding hydroxyl functional polyesters. This characteristic of the carboxyl polyesters is expected to

15 improve the storage stability of the corresponding powder coatings. T_g s for the polyesters were reported for the second heating cycle via Differential Scanning Calorimetry (DSC) at a scanning rate of 10°C/minute. The second heating cycle involved heating the samples to a

20 melt and then cooling the resin prior to measuring the T_g .

No crystallization or melting peaks were noted on the DSC curves of polyesters derived from NPG or the NPG/PDO

mixtures, indicating amorphous polyester (Figure 2). However, the polyester from pure PDO was a semi-crystalline polymer with crystallization and melting temperatures of about 112 and 180°C, respectively.

5 Therefore, partially replacing NPG with PDO up to 50 molar percent provided amorphous polyesters suitable for coating applications. It should be noted that the carboxyl polyesters were similar to the hydroxyl polyesters with respect to amorphous characteristics.

Table 3
Carboxyl Functional Polyesters Properties

Set	CPE00	CPE15	CPE30	CPE50	CPE100
NPG/PDO (mole)	100/0	85/15	70/30	50/50	0/100
Carboxyl Equivalent	529	534	545	545	530
Acid Number	106	105	103	103	105
Mn	2464	2579	2580	2238	--
Polydispersity	1.68	1.85	1.88	1.85	--
Colour Before Grinding	Slight yellow	Slight yellow	Slight yellow	Slight yellow	Slight yellow

10 Processability.

After premixing, the intimate powder mixture was continuously processed through a twin screw extruder to produce a uniform viscous melt. The extrusion
15 temperature was maintained at 75°C in zone 1 and 80°C in zone 2 at 50 rpm. All the powder mixtures from NPG and PDO polyesters were easily processed through the extruder (Table 4).

Table 4
Processability of Polyester Powder Coatings

Set	C00	C30	C50	P00	P30
Torque	73%	66%	60%	79%	74%
Temperature, zone 1 (°C)	75	75	75	75	75
Temperature, zone 2 (°C)	80	80	80	80	80
Processability	Good	Good	Good	Good	Good

Storage Stability.

5 The glass transition temperature of polyester resins for powder coatings should be high enough to achieve good storage stability. Commercially available polyesters for polyester/epoxy hybrid powder coatings typically have T_g values around 50 to 60°C. As expected, the powder
10 coatings formulated with up to 50 percent PDO derived carboxyl polyesters had very good storage stability, since they had T_g values over 55°C.

Storage stability tests were performed by placing powders in a capped jar at 40°C for 10 days. The powders
15 were subsequently examined each day for 10 days for free-flowing properties or lumps not easily broken. All samples had free-flowing properties after 10 days.

Inclined Plate Flow.

20 The inclined plate flow was measured according to the PCI standard method. It is a useful indicator of the degree of flow occurring during the curing of powder coated parts. The inclined plate flow is related to the zero shear melt viscosity of the base resin and is
25 influenced by the reactivity of crosslinking agent with the polyester resins. It was very clear that the plate flow increased with increasing PDO concentrations in the

PDO/NPG mixtures at both 175°C and 190°C (Table 5). For instance, the inclined plate flow was 50, 68, and 79 mm for pure NPG, 30 percent, and 50 percent PDO levels, respectively. Therefore, incorporation of PDO improved the flow properties of the powder coatings. The powders also had higher plate flows at 175°C than at 190°C, because of higher reaction rates at higher temperatures.

Gel Time Reactivity.

Gel time reactivity is the time required for a powder to advance to a gelled state through a liquid phase at a defined temperature. The test was performed via rubbing the powder coating with the tip of a wooden applicator stick over a hot plate until a solid gel was produced. Gel times for polyester powder coatings were determined at 180°C according to the PCI standard method. As seen in Table 5, all the coatings provided similar gel times, which is in accord with DSC studies.

Table 5
Inclined Plate Flow Test Results

Set	C00	C30	C50	P00	P30
PDO%	0	30	50	0	30
Flow at 175°C (mm)	64	85	104	22	23
Flow at 190°C (mm)	50	68	79	13	15
Gel time at 180°C (seconds)	280	270	290	340	320

Reactivity of Powders.

The reactivity of the carboxyl functional polyester polymers with epoxy resin crosslinking agents was studied via Differential Scanning Calorimetry (DSC) at a scanning rate of 10°C/minute. The DSC curves shown in Figure 3, and the testing results shown in Table 6 indicate the

onset of cure--exothermal peak and enthalpy are very close the powder coatings. Thus, polyesters based on NPG and PDO/NPG mixtures have similar reactivity with the crosslinking agent.

5

Table 6

DSC Results of the Reactivity of Powders

Set	C00	C30	C50
PDO%	0	30	50
Onset Temperature (°C)	110	108	111
Peak (°C)	178	180	180
Enthalpy (J/g)	61.61	60.36	62.34

Impact resistance.

10

The front and reverse impact resistance of the powder coatings were determined according to the ASTM D2794 standard method. The results in Table 7 indicated that PDO significantly improved the flexibility of both polyester/epoxy hybrid clear and pigmented powder coatings. For instance, the impact resistance increased from 5.65/3.39 m.N (50/30 in-lbs) (front/reverse) for the coatings based on pure NPG polyester to 11.30/7.91 m.N (100/70 in-lbs) for 30% PDO and to 78.08/18.08 m.N (160/160 in-lbs) for 50% PDO derived polyesters at a film thickness around 0.064 mm (2.5 mils). Moreover, the impact resistance was strongly dependent on the film thickness with thicker films having less flexibility.

15

20

Table 7
Front/Reverse Impact Resistance of Polyester/Epoxy
Hybrid Powder Coatings

Film Thickness mm (mil)	C00 m.N (in.lb.)	C30 m.N. (in.lb.)	C50 m.N (in.lb.)	P00 m.N (in.lb.)	P30 m.N (in.lb.)
0.028-0.030 (1.1-1.2)	--	--	--	5.65/1.36 (50/12)	9.04/3.39 (80/30)
0.038-0.041 (1.5-1.6)	12.43/10.17 (110/90)	16.95/14.69 (150/130)	18.08/18.08 (160/160)	--	--
0.043-0.046 (1.7-1.8)	--	--	--	3.16/0.68 (28/6)	5.65/1.58 (50/14)
0.061-0.064 (2.4-2.5)	5.65/3.39 (50/30)	11.30/7.91 (100/70)	18.08/18.08 (160/160)	--	--

Gloss

20 and 60 degrees gloss of the polyester/epoxy clear and pigmented powder coatings is presented in Figure 4. Incorporation of PDO gave slightly better gloss than pure NPG for clear coatings. Pigmented coatings containing polyesters with 30% PDO and 100% NPG had similar gloss values.

Hardness, Adhesion, and MEK Double-Rub Resistance.

All coatings evaluated had excellent adhesion to cold rolled steel substrates (Table 8). They passed the crosshatch tape adhesion test in accord with ASTM D-3359-92 with a value of 5B, i.e. without failure. Replacing NPG with PDO had little effect on the final pencil hardness. In the case of MEK double rub resistance, 50% PDO gave slightly lower values than the 30% PDO and pure NPG. Therefore, coatings based on PDO/NPG mixture combined good film hardness, impact flexibility with high gloss, and excellent adhesion.

Table 8

Hardness, Adhesion and MEK Double-Rub Resistance Properties

Properties	C00	C30	C50	P00	P30
Film Thickness mm (mil)	0.038 (1.5)	0.038 (1.5)	0.041 (1.6)	0.038 (1.5)	0.036 (1.4)
Pencil Hardness	HB	HB	HB	2H	2H
Adhesion	5B	5B	5B	5B	5B
MEK Double-Rubs	50	50	46	75	75

Chemical and Stain Resistance.

Coatings exposed to 10% HCl, 10% NaOH, gasoline, and mustard for 24 hours had excellent acid and caustic resistance compared to the control. Gasoline has a very

slight effect after a 24-hour exposure. All the coatings exhibited very good stain resistance to mustard. It is apparent that the stain resistance is not only connected to the chemical resistance but also to the hardness of the coatings. Soft resins tend to stain more than the hard resins. PDO derived coatings had little effect on the pencil hardness and the chemical resistance, hence no effect on the stain resistance was observed (Table 9). The data is presented in the form of ratings with 10 representing no effect and 1 indicating the most severe deterioration.

Table 9

Chemical and Stain Resistance of Powder Coatings

	C00	C30	C50	P00	P30
10% HCl	10	10	10	10	10
10% NaOH	10	10	10	10	10
Mustard	10	10	10	10	10
Gasoline	9	9	9	9	9

15 Flexibility-Conical Mandrel Bend and T-Bend Test.

Conical mandrel bend tests were performed via bending the coating panels on a conical mandrel tester (Gardner Laboratory, Inc. 3.2 mm (1/8") diameter) over a period of 3 seconds. The testing results are listed in Table 10. All clear coating panels passed the test, i.e. no cracking. However, the pigmented coating formulated with pure NPG polyester showed about 6 mm cracking upon mandrel bending, while coating incorporation of 30 percent PDO derived polyester passed the test.

25 Flexibility measured via the T-bend test revealed that incorporation of 30 percent PDO provided a 1T

coating whereas pure NPG resulted in a 3T value. Coating containing 50 percent PDO provided very good flexibility with OT values. In the case of the pigmented coatings, pure NPG resulted in a 5T value compared to a 3T when 30 percent PDO was incorporated. Therefore, these results provide further data on the contribution of PDO to improved flexibility of the powder coatings.

Table 10
Conical Mandrel Bend and T-Bend Test Results

	C00	C30	C50	P00	P30
PDO%	0	30	50	0	50
Film Thickness mm (mil)	0.038 (1.5)	0.038 (1.5)	0.041 (1.6)	0.038 (1.5)	0.041 (1.6)
1/8" Conical Mandrel Bending	Pass	Pass	Pass	Cracking at 6 mm	Pass
T-Bend	3T	1T	0T	5T	3T

C L A I M S

1. A polyester powder coating composition formed by reacting:

- 5 a) a polyester resin formed by reacting one or more aliphatic glycols and one or more polycarboxylic acids and/or anhydrides, wherein the aliphatic glycol is comprised of 5 to 90% 1,3-propanediol on a molar basis, in the presence of an esterification catalyst and then endcapping the polyester with an endcapping agent to ensure that
10 the polyester has carboxyl chain ends; and
b) an epoxy resin crosslinking agent.

2. The powder coating composition of claim 1 wherein the 1,3-propanediol comprises from 10 to 50% of the aliphatic glycols.

15 3. The powder coating composition of claim 1 or 2 wherein the aliphatic glycol has a number average molecular weight of 62 to 500.

4. The powder coating composition of claim 1, 2 or 3 wherein the aliphatic glycol is selected from the group
20 consisting of 1,3-butylene glycol, 1,4-butylene glycol, ethylene glycol, diethylene glycol, 1,2-propanediol, 1,6-hexanediol, triethylene glycol, tetraethylene glycol, tripropylene glycol, tetrapropylene glycol, dipropylene glycol, 2-methyl-1,3 -propanediol, polycarbonate diols
25 having hydroxyl numbers of 56 to 168, dimeric fatty alcohols, and neopentyl glycol.

5. The powder coating composition of claim 4 wherein the aliphatic glycol is neopentyl glycol.

6. The powder coating composition of any one of the preceding claims further comprising minor amounts of
5 branching agents selected from the group consisting of trimethylol propane, trimethylol ethane, and pentaerythritol.

7. The powder coating composition of any one of the preceding claims wherein the polycarboxylic acids and/or
10 anhydrides are selected from the group consisting of saturated, unsaturated, aliphatic, and aromatic polycarboxylic acids and/or anhydrides.

8. The powder coating composition of claim 7 containing a polycarboxylic acid and/or anhydride which is selected
15 from the group consisting of phthalic, isophthalic, terephthalic, sebacic, maleic, fumaric, succinic, adipic, azelaic, malonic, dodecanedioic, trimellitic, pyromellitic, or mixtures thereof.

9. The powder coating composition of claim 8 containing
20 a polycarboxylic acid and/or anhydride which is selected from the group consisting of isophthalic, terephthalic, and trimellitic, or mixtures thereof.

10. A polyester powder coating composition formed by reacting:

25 a) a polyester resin formed by reacting a mixture of, neopentyl glycol and 1,3-propanediol, wherein the 1,3-propanediol comprises from 5 to 90% of the mixture on a molar basis, with a mixture of terephthalic acid and isophthalic acid, wherein
30 the ratio of terephthalic acid to isophthalic

acid is in the range of 90/10 to 50/50, in the presence of dibutyl tin oxide, and adding trimellitic anhydride to endcap the polyester; and

- 5 b) an epoxy resin crosslinking agent which is a diglycidyl ether of 2,2-bis(4-hydroxy phenyl) propane which has been reacted with bisphenol-A and has a weight per epoxy of 450 to 900.

1/2

Fig.1.

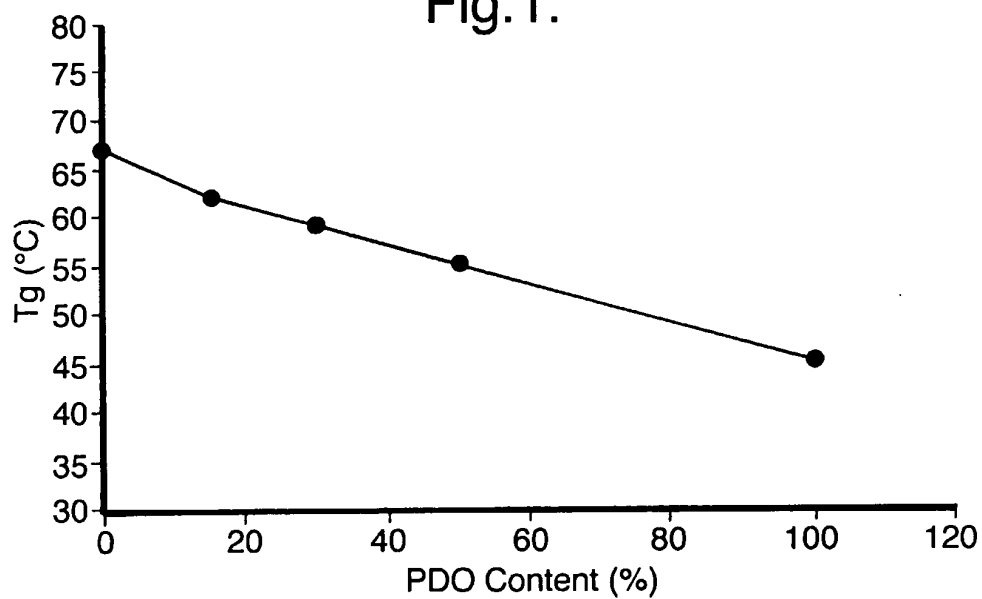
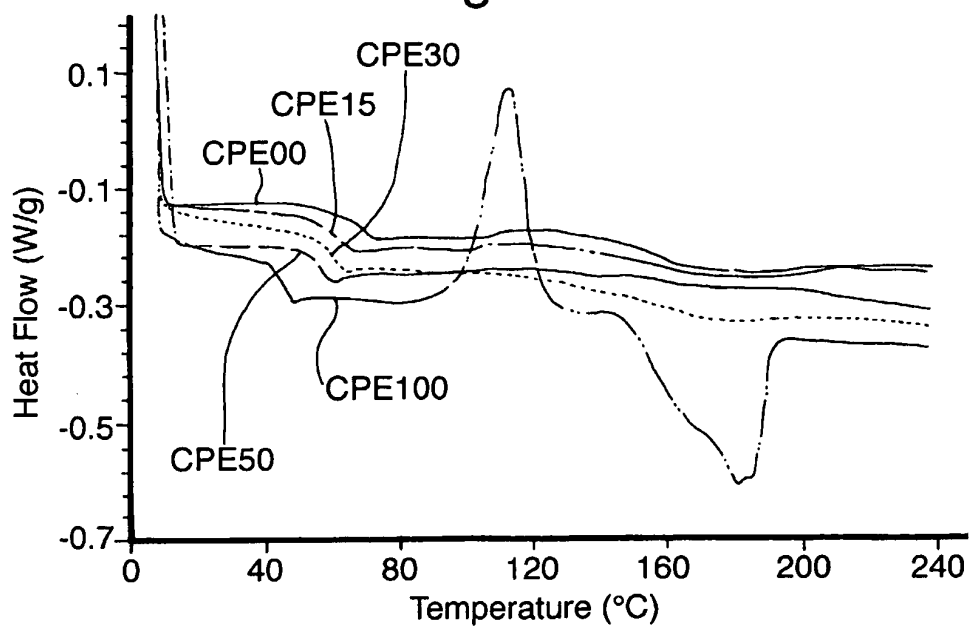


Fig.2.



2/2

Fig.3.

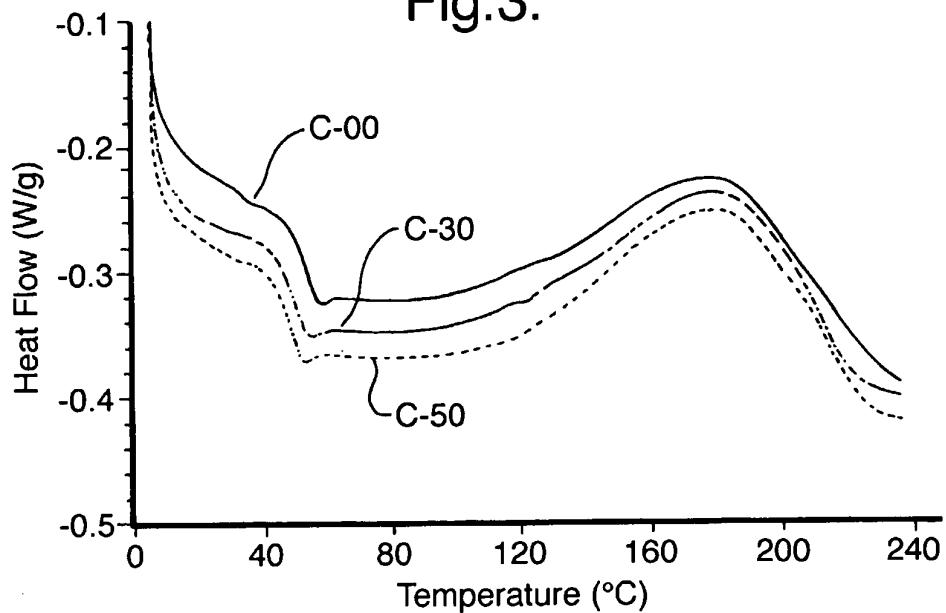


Fig.4.

